Introduction to Polymer Physics
Dr. Prateek Kumar Jha
Department of Chemical Engineering
Indian Institute of Technology-Roorkee

Lecture-59
Maxwell Model- I

Welcome. In the last lecture we have been talking about the oscillatory shear experiment in rheometer and how can we separate the liquid and solid contributions by doing rheological tests that essentially changes both the shear rate and shear in the same experiment and therefore allows to look at the two contributions especially in the case of viscoelastic materials. So, now I alluded already to the what is called a Maxwell model that is a phenomological model that we will use and I have given the motivation why are we doing it.

So, essentially what the Maxwell model is we assume that since the material a viscoelastic material possess both a liquid like feature and a solid like feature, we can think of it as dashpot connected in series with a spring which is being sheared in the system. So, if you do not know what a dashpot is think of like you have a bucket of viscous liquid and you are pulling something out of it and that will require a force to be applied so essentially if it is a viscous liquid we have to apply more force to pull it if it is less viscous liquid we apply less force to pull. In a sense it captures the viscous contribution spring on the other hand captures the elastic contribution because as I shear as I extend the spring the force is proportional to the extension. This has nothing to do with the actual polymer molecular system that we had in mind and this is the motivation that I have given in the last lecture that this is a yet another class of toy model that comes from a motivation from the experimental results since we know that the material possess a viscous and elastic behavior therefore we can think of a model like this that can still work. So, this is another class of toy models which are completely phenomological in nature.

So, in this case let us say if I am applying a net extension γ (t) that must be distributed with the extension or the shear of the spring. So, I am using the world extension and shear interchangeably but the idea is that in the experiment we are looking at the shear applied to a sample in this particular case it is very difficult to differentiate between the shear extensions because it is anyway toy model. The key idea is that we have something that takes care of elasticity in series with something that takes care of viscosity. So, this does not have a one-to-one counterpart in the polymer models that we have discussed.

So this will have extension or shear in the spring I represent the spring thing with e that tells it is the elastic part and the dashpot thing with t that tells it is the viscous part.

$$\gamma(t)=\gamma_e(t)+\gamma_v(t)$$

So, two of them must provide the net shear that of course if I pull it this way some of the shear is going into the spring some of that is going in the dash. The same thing applies for the shear rate if I am applying some then we have –

$$\acute{\gamma}(t)=\acute{\gamma}_c(t)+\acute{\gamma}_v(t)$$

and since the elements are in series what should also be the true is the net force that acts on the elements so this is a spring element and this is the dashpot element the net force acting on both these elements should be the same because they are essentially in series. You can think of an analogy with say current flowing with resistances in series. The amount of current that flows is essentially same if the elements are in series similarly here the amount of force that is acting on each of them are same and therefore the amount of stress is going to be the same. So, in that case this σ that will be a function of t will be some modulus of the spring element multiplied with γ_e of (t) + some viscosity of the viscous element multiplied with $\acute{\gamma}_v$ of (t). Therefore we have –

$$\sigma(t)=G_e\gamma_e(t)=\eta_v\acute{\gamma}_v(t)$$

And therefore we have essentially an elastic contribution and viscous contribution and therefore this model captures the viscoelasticity of the polymer. It is a very simple model but since we have incorporated an elastic element and a viscous element this would also possess an elastic behavior and viscous behavior and we will see that how this model that is coming from other phenomological origins with nothing to do with the polymer system gives you a good representation of what actually happens if I do experiments on a viscoelastic materials.

So, what we can note here is I can define a time constant τ that will be a ratio of the viscosity of the viscous element the dashpot element and the modulus of the elastic element and what we are going to elaborate is –

$$\tau = \frac{\eta_v}{G_e}$$

If‘ ‘t’ is much smaller than τ then the material would behave like a solid which has to be the case because solids have infinite viscosity and if ‘t’ is much higher than τ then this would behave like liquid. So, τ essentially determines how solid the material is if the materials is a perfect solid then the viscosity is very high so for all times of practical interest the system will behave like a solid. On the other hand if the material has a liquid feature it will have a lower value of viscosity and beyond that viscosity divided by the elastic constant we will start to see a liquid like behavior in the system essentially this timescale sets the two regimes of behavior one that is solid in nature and one that is liquid in nature depending on the amount of stress that is being applied.

So, let us say if we have a polymer sample and if I start shearing it in the very beginning its shows a solid nature but after some time it starts flowing and it becomes a liquid. So, the time it takes to become a liquid is determined by this τ and if the τ is smaller we will have a fast transition for the case of liquid. For the liquid phase and if the τ is higher we will have a very slow transition to the liquid phase but the assumption here is that all the materials become a liquid at infinite times and that is not really doing any harm to the analysis because we really do not go to infinite time. Okay.

So, now what we will do is we look at 2 or 3 different experiments that we have studied in the last couple of lectures and try to apply the Maxwell model in those cases and see whether it makes sense or not and if it does make sense that means that the model is a good approximation of the viscoelastic materials that we are interested in.

So, in the first example, we look at a step strain or a step shear that essentially goes like this where this is my time axis so it is 0 before and it is some $\dot{\gamma}$ afterwards the function can be written as –

$$\gamma(t)=\gamma_0\theta(t)$$

So, if it is a solid material then we know for solids the stress is proportional to the amount of shear and if it is a perfect solid then the modulus is also constant. So, for a solid we will expect a response that would be essentially simply like a perfect solid i.e. –

$$\sigma=G\gamma_0$$

If on the other hand if it is if it is say a Newtonian liquid then the stress is proportional to the shear rate now for the most part of it the shear rate is essentially 0 it was constant before time less than 0, it becomes constant after t higher than 0 only at time t = 0, there is a jump that would give rise to a very high shear rate. So, we will see an instantaneous spike at t = 0 apart from that everywhere the stress will be 0. So, in that case we are going to see something like that for Newtonian liquid.

$$\sigma=\eta\dot{\gamma}$$

In fact the first one applies to all solids with no liquid nature I want to emphasize this point over and over that the material may so a change in viscosity with time or a change in viscosity with applied shear but it may still not possess an elastic modulus. Similarly a solid may so a change in the elastic modulus with time or with applied shear but it may still not be viscous it will still be remain a solid. So, in all those cases we will not really think of them as viscoelastic a material that is not important in the case of polymers because polymers are inherently viscoelastic. So, these are all liquids with no solid nature so this is the kind of expectation we have.

Now let us imagine that what happens if it is a viscoelastic material so in that case what we may expect this again it is of course 0 before time t = 0 and the stress in the very beginning when I start applying the shear at that particular point you will have a solid like nature and then after the shear is applied then the material will start to flows it will take some time to start flowing even if it is a viscoelastic liquid and with even small even if it is like rather less viscoelastic that means it is more viscous more liquid like even then it will take some time to start flowing essentially what we will have is will start with a high stress and then the stress will fall down if it is a viscoelastic liquid and if you believe the Maxwell model τ should set the scale on when this happens.

If it is a solid that does not quite flow like a liquid then the stress will remain I went towards the very end and we will have a behavior may be something like this. The only difference here is that a viscoelastic solid retains certain elastic modulus even at long times a viscoelastic liquid perfectly becomes a liquid the stresses completely relax to 0 as the time proceeds.

So, this experiment I can think of as some sort of and stress relaxation and the way to think about it is like at time t = 0, I start applying stress and the material find ways to relax that stress. So, the material may relax if it is a liquid it can dissipate into some flow or deformation of material that will lead to the relaxation of the material. If on the other hand if it is a solid then the stress will remain as it is that relaxation will not really happen. If it is a viscoelastic liquid or solid then in that case the relaxation will take certain timescale to occur and that timescale is dictated by τ in the Maxwell model.

So, let us see how actually we get the result if I apply the Maxwell model in this case. The Maxwell model tells you is that –

$$\gamma(t)=\gamma_e(t)+\gamma_v(t)$$

When t > 0

$$\gamma_0=\gamma_e(t)+\gamma_v(t)$$

Also the stress would be –

$$\sigma(t)=G_e\gamma_e(t)=\eta_v\dot{\gamma}_v(t)$$

Now –

$$G_e \gamma_e(t) = \gamma_0 - \gamma_v(t)$$

Therefore –

$$\eta_v \dot{\gamma}_v(t) = G_e[\gamma_0 - \gamma_v(t)]$$

$$\frac{\eta_v}{G_e}\frac{d\gamma_v}{dt} = \gamma_0 - \gamma_v(t) \, so, \tau \frac{d\gamma_v}{\gamma_0 - \gamma_v(t)} = dt$$

Now we have to be careful about the limits. So, we go from time 0 to t at time t = 0 the $\gamma_v(0)$ has to be = 0 and the reason why is because ultimately we equate the

$$\sigma(t) = \eta_v \dot{\gamma}_v(t)$$

So at time t = 0, we start with no extension we get a shear rate that will take some time to develop some shear in the material. So, in the very beginning there is no shear on the other hand for the case of the elastic element we will we have something like this-

$$\sigma(t) = G_e \gamma_e(t)$$

So as soon as we apply the stress you get the strain in the material in the case of a liquid by application of stress we get a rate of strain or a rate of shear. So, the shear itself will take some time to develop. So, we can start from 0 to a final value γ_v of t and this if I solve what we get is –

$$\tau \ln\left[\frac{\gamma_0 - \gamma_v(t)}{\gamma_0}\right] = -t$$

$$\gamma_0 - \gamma_v(t) = \gamma_0 e^{\frac{-t}{\tau}}$$

Therefore,

$$\gamma_v(t) = \gamma_0\left[1 - e^{\frac{-t}{\tau}}\right]$$

So, once we have got this we can also get the other the extension in the elastic element by using the assumption that we have made here. So, the extension in the elastic element γ_e (t) will simply be –

$$\gamma_e(t)=\gamma_0-\gamma_v(t)=\gamma_0 e^{\frac{-t}{\tau}}$$

So, let us look at these functions that we have evaluated. So, if I look at the terms here what we have is –

$$\gamma_v(t)=\gamma_0\left[1-e^{\frac{-t}{\tau}}\right]$$

$$\gamma_e(t)=\gamma_0 e^{\frac{-t}{\tau}}$$

$$\dot{\gamma}_v(t)=\frac{\gamma_0}{\tau}e^{\frac{-t}{\tau}}$$

$$\dot{\gamma}_e(t)=\frac{-\gamma_0}{\tau}e^{\frac{-t}{\tau}}$$

And if I want to find the stress tensor I can use any of these two formulas-

$$\sigma(t)=G_e\gamma_e(t)=\eta_v\dot{\gamma}_v(t)=G_e\gamma_0 e^{\frac{-t}{\tau}}$$

Let us say if I use the first one this is $G_e\gamma_0 e^{\frac{-t}{\tau}}$ and we can see why these two will give you the same answer by simply plugging in the values the first one is $G_e\gamma_0 e^{\frac{-t}{\tau}}$ and the second one is η_v γ_0 by $e^{\frac{-t}{\tau}}$.

$$G_e\gamma_0 e^{\frac{-t}{\tau}}=\eta_v\frac{\gamma_0}{\tau}e^{-t}$$

$$\frac{\eta_v}{G_e}=\tau$$

So, now if I plot these functions with respect to time and I am only doing for time t higher than 0 what we are going to notice here is that if I look at if I look at the stress, the stress will start with a high value this is this particular function. So, at time t = 0 we have a value $G_e \gamma_0$ and this value with decay to 0 and the rate of decay is dictated by the time scale τ essentially it is the first order decay or exponential decay. If I look at if I look at the extension of the viscous element or the shear on the viscous element at time t equal to 0 the exponential function is 1. So, it will start from 0 and then eventually at infinite time the exponential term is going to be 0. So, it will become γ_0 so this essentially will so a behavior like this $\gamma_e(t)$ on the other hand will start from γ_0 and then it will decay to 0. So, while the shear or the extension of the viscous element is increasing with time the shear or the extension of the elastic element is decreasing with time and the same thing we can also look at in its derivatives. So, if I look at $\dot{\gamma}_v$ t it will start with a large number, that is γ_0 by τ but this will decrease with time on the other hand if I have $\dot{\gamma}_e(t)$ it will start with a large number but it is negative and it will increase with time eventually it becomes 0 this is also $-\gamma(t)$.

You can see how it works in all the time scale everywhere is essentially tau and we can see like well how exactly that fits well into the picture that we have discussed earlier at ‘t’ much higher than τ we have a liquid behavior and for t much smaller than tau we have a solid behavior.

You can see if I start looking at from the first plot of the stress the material in the beginning has a stress and that stress relaxes with times eventually when it becomes a liquid that stress has dropped down to pretty much 0. If I look at the shear or extension of the viscous element at time t = 0, it is starts from 0 by the jump what we have showed earlier and then it starts increasing but the rate of increase is decreasing with time and eventually it settles to a final value. So, you cannot really shear a liquid beyond a final steady state γ_0 value because in any case that is the applied shear on the entire sample.

On the other hand as soon as we apply the stress you will have a shear γ_0 because on the elastic element because stress is proportional to the strain but since the stress is decreasing with time the shear of the elastic element is also decreasing with time and eventually it also goes to 0. The same things are explained by the rates so the rate of decay of the elastic element is essentially decreasing that is what we see here and the same is true for the viscous element as well. The only difference is that the viscous element has started from 0 so it is increasing in the amount of shear. On the other hand the elastic element has started from a highly positive value so it is decreasing in the amount of shear and eventually it becomes a liquid.

So, depending on when are we looking at if I look at a very short time what you will notice is that if I look at say small times that are before τ what we can notice is that the material has a stress and therefore the material has a significant shear in the elastic element and therefore the material also has a significant shear rate for a constant strain applied and it also has a significant the shear rate in the elastic element as well but if we go to longer times then at longer time's right here the stresses have dissipated since we apply a constant strain the strain rate or shear rate is 0 and therefore the material will stop flowing and the material will pretty much relax its stress to 0 that will not be the case if I do a constant shear rate experiment that is what I will show next.

So, next in the next lecture we will repeat the same kind of example for the case of a constant shear rate and we will see like how the behavior of system changes and how the Maxwell model still works in that case and therefore we can claim that the Maxwell model is a good starting model at least to look at the viscoelastic behavior of systems.

I conclude with this, thank you.